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Optical, thermal, dielectric and mechanical studies on glycine doped potassium dihydrogen orthophosphate singles crystals grown by SR method

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Abstract

Single crystals of glycine doped potassium dihydrogen orthophosphate (KDP) were grown by Sankaranarayanan-Ramasamy (SR) method with have a size of 20 mm in diameter and 90 mm in length. The grown crystals were subjected to powder X-ray diffraction (XRD), differential scanning calorimeter (DSC), thermo-gravimetric analysis (TGA), optical transmission, dielectric and Vickers microhardness studies. The TGA of the samples reveal that the grown crystals were stable up to 200 ˚C at least for all samples. The important optical parameters such as reflection and extinction coefficients of the grown crystal were calculated and discussed. The variation of dielectric constant, dielectric loss, a.c. resistivity and a.c. conductivity with frequency of applied field in the range from 1 kHz to 200 kHz was studied. The lower values of dielectric loss due to less of defect were observed in SR grown glycine doped KDP crystals. Vickers microhardness study shows higher mechanical stability in SR method grown crystals.

Keywords: Growth from solutions; Nonlinear optical materials; Dielectric materials

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1. Introduction

Nonlinear optical (NLO) crystals with high conversion efficiencies for second harmonic generation are desirable in various applications such as telecommunication, optoelectronics and laser technology. There have been interesting materials both academically and industrially. KDP is a dielectric material well

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known for its nonlinear optical and electro optical (ferroelectric at low temperature : T_c = 123 K) properties [1-2]. The excellent properties of KDP include transparency in a wide region of optical spectrum, resistance to damage by laser radiation and relatively high nonlinear efficiency, in combination with reproducible growth to large size. Therefore, it is commonly used in several applications such as laser fusion, electro-optical modulation and frequency conversion [3]. Many studies on the growth and properties of KDP crystals in the presence of impurities have been reported [4-7]. The amino acids are the famous organic materials, play a vital role in the field of nonlinear optical crystal growth. Since most of the amino acids exhibit NLO property, it is of interest to dope them in KDP [8]. With the aim of discovering new useful materials for academic and industrial use an attempt has been made to modify KDP crystals by adding some amino acids. KDP doped with amino acids like L-glutamic acid, L-histidine, L-valine were reported [9]. There were found modifications in optical, electrical and mechanical properties. Furthermore, microelectronics industry needs new low dielectric constant (ε_r) materials as an interlayer dielectric (ILD) because lowering the value of dielectric constant of the ILD decreases the RC delay and lowers power consumptions [10]. Some substances when doped to KDP may yield KDP with low dielectric constant [10-11]. Glycine was attempted as the dopant to reduce dielectric constant and modify KDP crystals. There are reported [12] that the second harmonic generation efficiency is found to be appreciably increased by addition of amino acid glycine as impurity in KDP crystals grown by conventional method. The growth of bulk size crystals without defects is a challenging task for crystal grower. The Sankaranarayanan-Ramasamy (SR) method gives bulk unidirectional crystals with good quality from solution [13]. The SR growth technique is suitable to get unidirectional crystals from solution. The main advantages of SR solution growth technique are simple experimental setup, unidirectional growth, high solute-solid conversion, minimum thermal stress on the crystal during growth and prevention of microbial growth [14]. Recently many papers show that the SR method grown crystals have higher crystalline perfection than conventional grown crystals [15-17]. There are no reported on the effect of glycine on unidirectional crystals growth by SR method. Studies on the frequency and temperature dependence of dielectric properties unveil useful information about structural changes, defect behavior and transport phenomena [18]. In this paper the growth by SR method of glycine doped KDP crystals are reported. The grown crystals were characterized using XRD, TG/DSC, UV-vis NIR, dielectric constant, dielectric loss and Vicker microhardness to reveal the structure, thermal properties, optical transmittance, dielectrics, defects and mechanical strength of the SR grown glycine doped KDP crystals.

2. **Experimental**

2.1. Crystal growth

Analytical reagent grade (AR) samples of KDP and glycine along with de-ionized water were used for the growth of single crystals. After two time of recrystallization, the solution was prepared in slightly undersaturation condition at 30 °C. The mixture was thoroughly stirred for 6 h for homogenization. The glycine of different mole concentrations (1 mole %, 2 mole % and 3 mole %) doped KDP solution was filtered using No.1 whatman filter paper. Then the solution was poured in a different beaker in the water-bath with constant temperature at 35 °C. The KDP crystals doped with glycine were crystallized by slow evaporation method. Seed crystals of pure and doped KDP were formed due to spontaneous nucleation. Good quality seed crystals were collected for growing large size crystals by SR method. The SR method [13] was employed to grow glycine doped KDP single crystals using controllable ring heaters, transparent glass tubes. Two ring heaters are positioned in the top and bottom of ampoule and connected to temperature controller. The <001> direction of the seed crystal was selected for unidirectional crystal growth. A seed crystal was mounted at the bottom of the ampoule. The temperature difference between the top and bottom heating coils was carefully maintained. After a time spanned 20 days, good quality single crystal of doped KDP were grown successfully with size ~90 mm length and ~20 mm diameter.

2.2. Characterization

In the present study, powder X-ray diffraction analysis has been carried out using D5005 X-ray diffractometer (Bruker AXS) with CuK_{α} (λ=1.5418 Å). The sample was scanned over 10-70 degrees at the rate of 1 degree/min. Thermal analysis was carried out on the crushed specimen of the SR method grown crystals by employing a Differential Scanning Calorimeter (Mettler Toledo DSC822) and Thermo-gravimetric Analyzer (Mettler Toledo TGA/SDTA 851) at 15 ˚**C**/min heating rate in the nitrogen atmosphere. Optical transmission spectra were recorded for the grown crystals using HITACHI U-1800 UV-Vis spectrometer. Doped KDP samples were cut to a proper thickness and polished. Each sample was electroded on both sides with high purity silver paste so that it behaved like a parallel plate capacitor for dielectric study. Dielectric constant and loss were measured using LCR-800 series (Good Will Instrument) multifrequency LCR meter. Microhardness studies were made on the permanent (001) plane of both the conventional and SR method grown crystals using a Anton-Paar MHT-10 microhardness tester. Load of different magnitudes were applied. The indentation time was fixed as 10 s for each trial.

3. Results and discussions

3.1. X-ray diffraction

Powder XRD studies of the doped KDP crystals grown by both conventional and SR methods confirmed the tetragonal structure of the grown crystals. Results were compared with the JCPDS database where the prominent peaks of the reported values coincided with the investigated patterns. The crystals were identified by comparing the interplanar spacing and intensities of the XRD pattern with the JCPDS data of KDP crystals. Pure KDP crystals belong to scalenohedral class of tetragonal system having unit cell with lattice parameters a = b = 7.448 Å and c = 6.977 Å [19]. The SR method grown crystal of glycine doped KDP has the unit cell parameters, a = b = 7.604 Å and c = 6.985 Å. The slight shifts in the 2θ values of the doped crystals suggest that its structure was slightly disturbed compared to the pure KDP crystals.

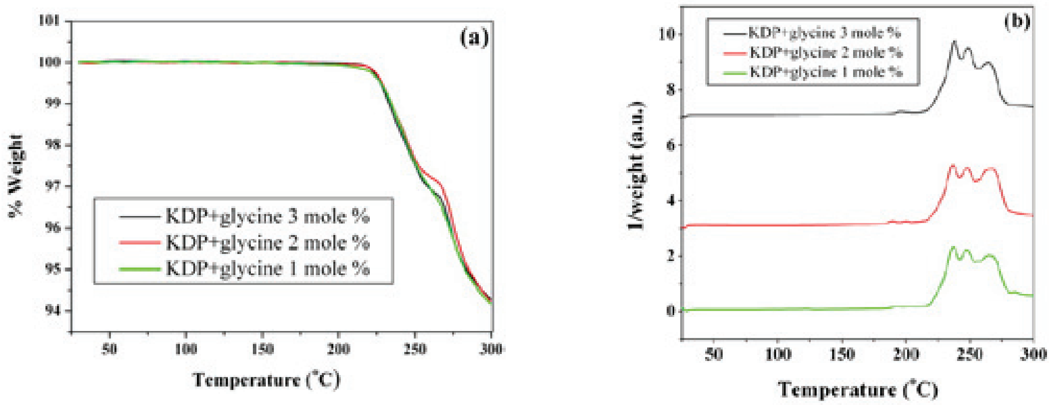


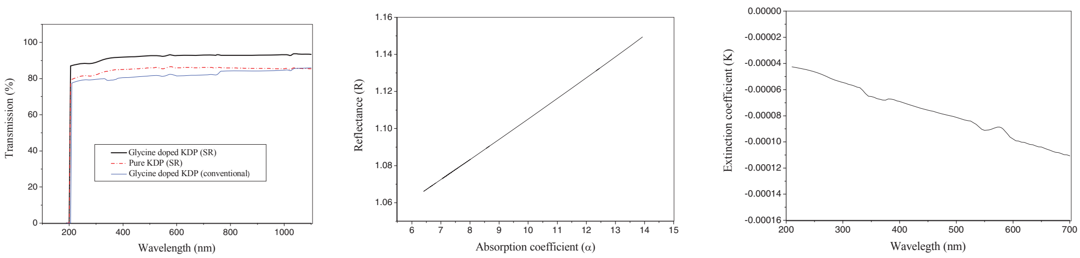
Fig. 1. (a) Thermogravimetric Analysis (TGA) and (b) Differential Scanning Calorimetry (DSC) data of the SR method grown crystals of KDP doped with 1 mole %, 2 mole % and 3 mole % of glycine

3.2. Thermal studies

Differential scanning calorimetry is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to the sample than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. Figure 1 (a) illustrates the thermo-gravimetric analysis for the doped KDP crystals grown by SR method. The TGA of the samples indicate that they are stable up to 200 ˚**C** at least for all samples and short weight loss is at temperature near 210 ˚**C**, it may be due to physically adsorbed water. The weight loss in the temperature 230 - 300 ˚**C** is probably due to the decomposition of the KDP and amino acid glycine. Figure 1 (b) shows the DSC spectra for the glycine doped KDP crystals grown by SR method. It is found that there are three endothermic peaks at 236 ˚**C**, 248 ˚**C** and 266 ˚**C**.

3.3. Optical property studies

The recorded transmittance spectra of pure and 1 mole % glycine doped KDP crystals in the wavelength range 200-1200 nm are shown in Fig. 2. It can be seen that the crystals have sufficient transmission in the entire visible and near Infrared region. The cut off wavelength is almost same (~200 nm) for pure and doped KDP crystals. The glycine doped KDP crystal grown by SR method has transmittance up to 90% in the higher wavelength region and it has 5% higher transmittance than the pure KDP crystal. The result shows that the SR method grown crystal has higher quality than the conventional method grown crystal.



(a) (b) (c)

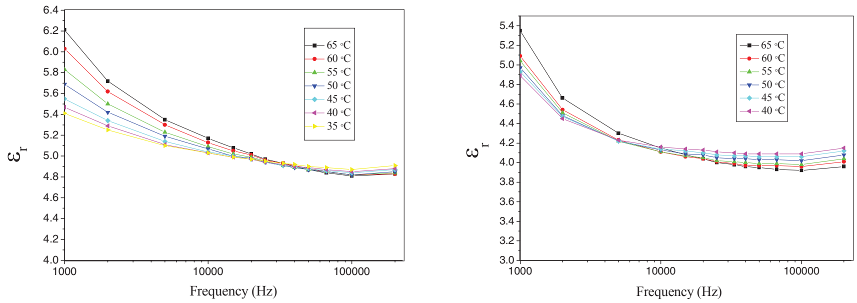
Fig. 2. (a) UV-vis NIR spectrum of 1 mole % glycine doped KDP crystals; (b) Plot of reflectance versus absorption coefficient; (c) Plot of extinction coefficient versus wavelength

3.4. Dielectric studies

Dielectric properties are correlated with electro-optic properties of the crystals particularly when they are nonconducting materials. Permittivity characterization may yield some useful initial information. The glycine doped KDP crystals grown by SR method have been characterized by dielectric constant studies. The dielectric constant (ε_r) was calculated using the relation:

$$\varepsilon_r = \frac{Cd}{A\varepsilon_0} \qquad (1)$$

where C is the capacitance, d is the thickness of the sample, A is the area of the face in contact with the electrode and ε_0 is the permittivity of free space (8.854×10^{-12} F/m).



(a) (b)

Fig. 3. Frequency dependence of dielectric constant at different temperatures of 1 mole % (a) and 3 mole % (b) glycine doped KDP crystals grown by SR method

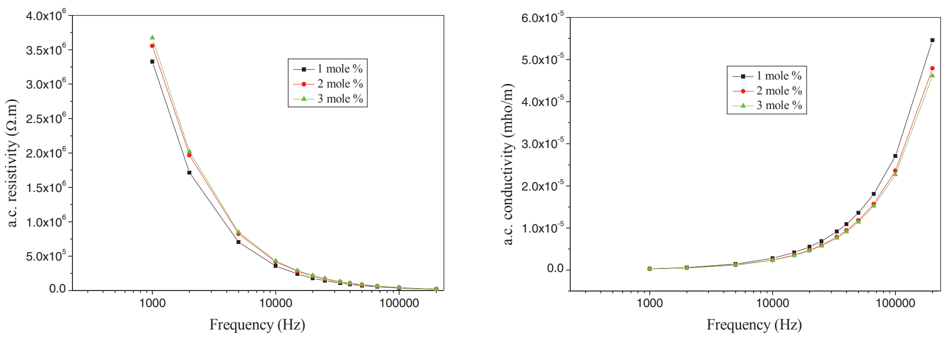
Figure 3 shows the dielectric constant with different frequencies for the SR method grown crystals of glycine doped KDP. It is observed that the dielectric constant decreases with the increasing of frequency up to 50 kHz. After that the dielectric constant remains almost constant at higher frequencies. The magnitude of dielectric constant depends on the degree of polarization charge displacement in the crystals. Dielectric constant is found to increase with temperature at low frequencies (1-10 kHz) but decrease with temperature at higher frequencies (more than 10 kHz). The a.c. resistivity and a.c. conductivity have been calculated using the relations :

$$\rho = A/2\pi fCd \quad \text{and} \quad \sigma = 1/\rho \tag{2}$$

where C is the capacitance, d is the thickness, A is the area of the crystal and f is the frequency of the applied field. The variation of a.c. resistivity and conductivity with the frequency of applied field is shown in Fig. 4 (a) and (b), respectively.

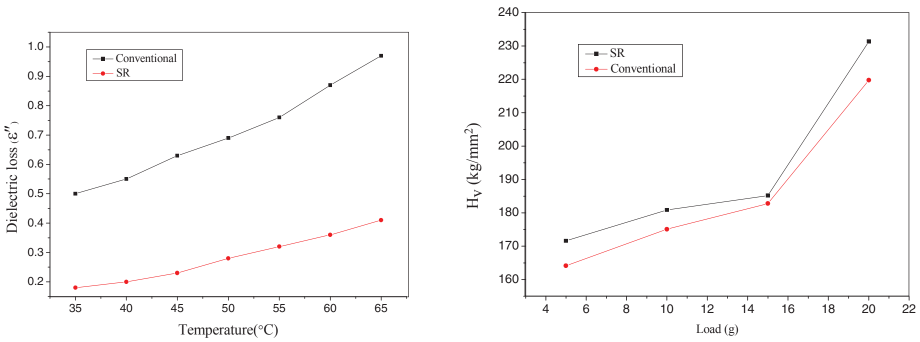
The loss tangent ($\tan\delta$) is a parameter of a dielectric material that quantifies its inherent dissipation of electromagnetic energy. The dielectric loss (ε'') was calculated from loss tangent using the relation:

$$\varepsilon'' = \tan\delta . \varepsilon_r \tag{3}$$



(a) (b)

Fig. 4. Frequency dependence of resistivity (a) and conductivity (b) at 35 °C of 1 mole % glycine doped KDP crystals grown by SR method



(a) (b)

Fig. 5. (a) Temperature dependence of loss tangent at 10 kHz of 1 mole % glycine doped KDP crystals (b) Vickers microhardness of 1 mole % glycine doped KDP crystals

3.5. Microhardness testing

The hardness of a material is a measure of its resistance to plastic deformation. The Vickers microhardness number (H_v) was calculated using relation:

$$H_v = \frac{1.8544P}{d^2} \text{ (kg/mm}^2\text{)} \qquad (4)$$

where P is the indenter load (kg) and d is the diagonal length of the impression (mm). The plot of Vickers hardness versus load for the conventional and SR methods grown doped KDP crystals is shown in Fig. 5(b). It is seen that the hardness value for the SR grown crystal is higher than the hardness of the conventional method grown crystal. Larger hardness value for the SR method grown KDP crystal doped with glycine indicates greater stress required to form dislocation thus confirming greater crystalline perfection.

4. Conclusions

Bulk single crystals with large size of glycine doped KDP have been grown by SR method. The crystal structure was confirmed by XRD study. The TGA shows that the grown crystals are stable up to 200 ˚**C**. The DSC investigation indicated that the measured enthalpy values depend on the concentration of the dopant. The optical transmission analysis revealed that glycine doped KDP crystals have very high percentage of transmission in the entire visible region, which is very essential for NLO crystals. The 1 mole % glycine doped KDP grown by SR method has 5% and 10 % higher transmittance than the pure KDP crystal grown by SR method and the crystal grown by conventional method respectively. The optical parameters such as reflection and extinction coefficients were calculated and indicated that the grown crystal posses enhanced optical quality. The lower values of dielectric constant on doping glycine were observed. The a.c. conductivity increases with frequency, obviously reverse trend was observed for the a.c. resistivity. The reduction in the values of a.c. conductivity on doping glycine is due to the basis of the impurity presence in form of doping and the L-defects. Low dielectric loss is obtained for the SR method grown doped KDP crystal compared to the crystal grown by conventional method. The low values of dielectric loss indicate that the grown crystal contains minimum defects. Vicker microhardness measurements also indicate that the crystals grown by the SR method have good crystalline perfection and low density of defects, which is very essential for various applications.

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